

**X-ray Photoemission Measurements and Electronic Structure of
 $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$**

R. P. Vasquez

**Center for Space Microelectronics Technology
Jet Propulsion Laboratory, California Institute of Technology
Pasadena, California 91109-8099**

M. Rupp and C. C. Tsuei

**IBM Research Division, T. J. Watson Research Center
Yorktown Heights, New York 10598**

Abstract

$\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ (Hg-1212) thin films grown epitaxially on SrTiO_3 (100) substrates have been chemically etched and studied with x-ray photoelectron spectroscopy (XPS). The XPS data presented here are the first on an **epitaxial** thin film of a mercury **cuprate** superconductor, the first in which signals from the superconducting **phase** dominate **all** the core level spectra, and the first to exhibit a clear Fermi edge in the valence band region. **Hg** is found to be in a single chemical state, contrary to previous reports based on measurements from **sintered polycrystalline pellets**. The Ba, Ca, Cu, and O core levels are similar to those measured from $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Tl-2212), which is chemically and structurally most similar to **Hg-1212**, and other **cuprate** superconductors. Despite the similarities in the core level spectra, distinct differences are observed in the valence bands of **Hg-1212** and **Tl-2212** which are attributed to differences in the apical oxygen densities of states.

Interest in Hg cuprate high temperature superconductors (HTS), $\text{HgBa}_2\text{Ca}_{1-n}\text{Cu}_n\text{O}_{2n+2+\delta}$ (Hg-1201, Hg-1212, and Hg-1223 for $n = 1, 2, 3$, respectively), has been stimulated by observations of higher superconducting transition temperatures, T_c , than are observed for other cuprates ($T_c \sim 95$ K for Hg-1201, $T_c = 125$ K for Hg-1212, and $T_c = 135$ K for Hg-1223 at ambient pressure).^{1,2} It has also been found that T_c can be increased to over 150 K when these materials are placed under quasi-hydrostatic pressure.³ In addition, the recent growth of high quality Hg-1212 epitaxial thin films⁴ and the fabrication of these films into superconducting quantum interference devices (SQUIDs)⁵ which operate at temperatures in excess of 110 K demonstrates the potential technological importance of these materials.

X-ray photoelectron spectroscopy (XPS) has been utilized to characterize the chemical states of the component elements and the valence band densities of states in numerous studies of HTS materials.⁶ Among the results of previous studies of HTS materials are a set of well-defined spectral features which are characteristic of high quality surfaces:^{7,8} a high binding energy Cu^{+2} satellite in the Cu 2p core level region, low binding energy O 1s (528 -529 eV) and alkaline earth core level signals with little or no intensity at higher binding energies, and a clear Fermi edge in the valence band region. These studies on HTS materials which are chemically and structurally similar to the Hg cuprates should provide valid guidelines for judging the quality of the XPS measurements. XPS measurements on Hg-1212 and Hg-1223⁹ and on Hg-1201¹⁰ have previously been reported. In one study only Cu 2p and Hg 4f core level measurements were presented,¹⁰ so that it is not possible to assess the surface cleanliness. In the other study,⁹ a complete set of core level measurements was presented. Spatially variant chemical inhomogeneities and differential sample charging were reported, and the spectra included prominent, or even dominant, signals which were attributed to nonsuperconducting grain boundary species. Both of these previous studies^{9,10} mentioned valence band measurements, including a report of a weak Fermi edge,¹⁰ which were not presented. Higher quality XPS data for Hg cuprates are clearly desirable.

In this work, XPS measurements are reported for a Hg-1212 epitaxial thin film, for which signals from grain boundary species are not expected to be as severe a problem as it is for sintered powders. Core level measurements are presented which are dominated by signals attributable to the superconducting phase, and are compared to those measured from $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Tl-2212), which is chemically and structurally most similar to Hg-1212. Measurements of the valence band of Hg-1212 which exhibit a clear Fermi edge are presented for the first time, and are compared to the measured valence band¹¹ of Tl-2212 and to the densities of states reported in Hg-1212 and Tl-2212 band structure calculations.^{12,13}

The Hg-1212 films are grown epitaxially on SrTiO_3 (100) substrates by laser ablation. Details of the film growth and characterization are described elsewhere.⁴ The film used for this study was one of a batch of four grown together, of which the other three all exhibited zero resistance at 120 K, and was ampouled for transport to the XPS spectrometer. The ampoule was broken in the inert ultrahigh purity nitrogen atmosphere of a dry box which encloses the XPS load lock area. The surface was cleaned in the dry box with a nonaqueous etchant consisting of 0.2% by volume Br_2 in absolute ethanol, rinsed in ethanol, blown dry with nitrogen and loaded into the XPS chamber with no air exposure. The etchant forms reaction products (HgBr_2 , BaBr_2 , CaBr_2 , CuBr_2) which are soluble in ethanol, and has yielded high quality surfaces for other HTS materials.⁸ The etch rate was determined to be $\sim 400\text{--}600 \text{ \AA}/\text{min}$. The XPS spectra are accumulated on a Surface Science Instruments SSX-501 spectrometer with monochromatized Al K_α x-rays (1486.6 eV) and a base pressure of 5×10^{-10} Torr. The x-ray beam diameter is $150 \text{ }\mu\text{m}$ for the core level measurements and $300 \text{ }\mu\text{m}$ for the valence band measurements, and the pass energy of the electron energy analyzer is 25 eV, parameters which yield a peak full width at half maximum (FWHM) of 0.7 eV for the Au $4f_{7/2}$ signal from a gold film. The photoelectron emission is normal to the sample surface. After completion of the XPS measurements, ac susceptibility measurements show a superconducting transition onset near 116 K with a transition width of 7 K, verifying that the film remains superconducting after transport, etching, and vacuum exposure.

XPS spectra measured **prior** to etching exhibit dominant high binding energy signals which are affected by differential sample charging, as determined by varying the filament current on an electron flood gun. Low binding energy **spectral** features attributable to the superconducting phase are also detectable as minor components. No charging is observed after etching, indicating that insulating surface phases are removed by the **etchant**. Small signals from the **SrTiO₃** substrate are observed even prior to etching, indicating that the film contains some voids, and increase in intensity with increasing etch time. Signals from the substrate could potentially affect measurements of the O 1s core level and the valence band (hybridized Cu 3d -O 2p states). This effect can be estimated from the **measured** Sr 3d and Ti 2p intensities and the photoelectric cross sections to be **<10%** of the total O 1s intensity and **<2%** of the valence band signal after 30s of etching, and approximately twice those levels after 60s. Accordingly, only spectra measured after 30s of etching are presented below, unless specified otherwise. **The measured stoichiometry** after etching is **Hg:Ba:Ca:Cu:O** \approx 0.6:2:1:2:8. The **Hg** deficiency is likely due to the volatility of Hg, while the excess O is **related** to contaminant species, as discussed and shown in the spectra below.

The O 1s signal, which is most commonly used to assess surface cleanliness, is shown in Fig. 1(a). The dominant peak near 528.5 eV is consistent with measurements from other HTS materials,⁸ and is thus assigned to the superconducting phase, and has a shoulder on the low binding energy side. The peak near 531.5 eV is dominant prior to etching and in previous measurements of Hg cuprates,⁹ and has been determined to originate from nonsuperconducting surface or grain boundary species in studies of other HTS materials.* This was verified in this work with angle-resolved measurements, in which the high binding energy signal is enhanced at grazing photoelectron emission angles. The O 1s signal measured from an etched Tl-2212 film¹⁴ is shown in Fig. 1(b) to be very similar to the spectrum in Fig. 1(a). The components of the spectra can be resolved in the second derivatives, as shown in Figs. 1(c) and 1(d). These components have binding energies of 527.8 eV and 528.7 eV for Hg-1212, and are assigned to

consistent with the assignment of the dominant C) 1s signal to grain boundary species in the same study.⁹ In this work, the intensities of the higher binding energy components are enhanced for a grazing photoelectron emission angle and are dominant prior to etching, and are therefore assigned to **nonsuperconducting** species. The lower binding energy signals, which are dominant after etching and assigned to **Hg-1212**, are virtually identical to those observed for Tl-2212.^{11*} These signals occur at significantly **lower** binding energies than those measured for **Ba** and **Ca** metals, an observation which is characteristic of the alkaline earth core levels for other HTS materials.¹⁸ Two **Ca** 2p doublets have also been observed for **Tl-2212** and **Bi₂Sr₂CaCu₂O_{8+δ}**,^{11,18} and have been interpreted as originating from cation disorder and occupation of inequivalent lattice sites.

The **Cu 2p_{3/2}** signal of Hg-1212, shown in Fig. 4, is typical of **Cu⁺²** compounds, with a high binding energy manifold corresponding to **d⁹** final state screening and a more intense peak at 933 eV corresponding to well-screened **d¹⁰** states resulting from ligand-to-metal charge transfer. This data is qualitatively similar to measurements in one earlier study,⁹ but differs from a study¹⁰ of **Hg-1201** scraped in vacuum, in which no signal corresponding to **d⁹** screening was observed. Scrape-induced surface **damage** of other HTS materials has previously been shown^{8,19} to result in loss of intensity in this spectral region due to reduction of **Cu⁺²** to **Cu⁺¹**. The same study¹⁰ also concluded that **Cu** occurred in +1, +2, and +3 oxidation states based on the observed **lineshape** of the **d¹⁰** signal. However, the shape of the **d¹⁰** signal results from a multiplet of final states rather than multiple oxidation states, as discussed in detail elsewhere.²⁰ The **Cu 2p_{3/2}** signal in Fig. 4 is similar to measurements of other HTS cuprates,^{8,20} though the **d⁹/d¹⁰** intensity ratio of 0.38 is slightly lower than the value of 0.45 observed for Tl-2212.¹¹ This difference may reflect differences in electron correlation in these similar materials.

Fig. 5 shows the **Hg 5d** and **Ba 5p** shallow core levels and the valence band of **Hg-1212**, which consists of hybridized **Cu 3d** and **O 2p** states. This is the first published valence band spectrum for a **Hg cuprate** superconductor. For the photon energy used in this study, the **Cu 3d** character is dominant (87% of the spectral weight assuming ideal stoichiometry) due to a higher

photoelectric cross section. Shown below the valence band is the **Cu 3d** partial density of states from band structure **calculations**,¹² shifted by 2.2 **eV** to approximately match the envelope of the measured density of states. Similar shifts have been found necessary for other HTS materials, and have been attributed to electron correlation effects which are inadequately treated in the calculations. The insets in Fig. 5 show the **Fermi edge measured** after 30s and 60s of etching, verifying the high quality of the data presented here.

The data presented above show that the core levels of **Hg-1212** are similar to those of other HTS cuprates, and are nearly identical to those measured for Tl-2212. However, despite the similarities observed in the **Hg-12,12** and Tl-2212 core levels and the chemical and structural similarities, distinct differences are observed in the valence bands, as shown in Fig. 6. The density of states at the Fermi level is lower for **Hg-1212** despite having a higher **T_c**. The **Hg-1212** valence band is also significantly broader on the high binding energy side. Although there are some differences in the **Hg-1212** and Tl-2212 **Cu 3d** partial densities of states,^{12,13} they do not appear to be sufficient to account for the data in Fig. 6 near 6 **eV** binding energy. The most notable differences occur for the apical oxygen 2p partial densities of states, shown below the valence bands in Fig. 6, which are qualitatively consistent with the differences observed in the measured valence bands. Both of the calculated spectra have been shifted by the ~2**eV** necessary to align the **Cu 3d** partial densities of states with the measured valence bands.

In summary, XPS has been used to characterize an **epitaxial** thin film of a mercury **cuprate** superconductor for the first time. Hg is found to be in a single chemical state, contrary to previous reports based on measurements from **sintered polycrystalline** pellets. The Ba, Ca, Cu, and O core levels are similar to those measured from other HTS **cuprates**, and are nearly identical to those of Tl-2212, which is chemically and structurally most similar to **Hg-1212**. Two O 1s signals assigned to Cu-O planes and Hg-O bonds are distinguishable, as are two Ca 2p signals which may be due to cation disorder. **These** are the first XPS measurements of a **Hg** cuprate in which signals attributable to the superconducting phase dominate all the core level spectra. Despite the

similarities in the core level spectra, distinct differences are observed in the valence bands of Hg-1212 and Tl-2212 which are consistent with differences in the calculated apical oxygen densities of states. This work presents the first published valence band spectrum of a Hg cuprate superconductor, and the first observation of a clear Fermi edge.

Part of the work described in this paper was performed by the Center for Space Microelectronics Technology, Jet Propulsion Laboratory (JPL), (California Institute of Technology, and was sponsored by the JPL Director's Research and Development Fund.

References

1. S. N. Putilin, E. V. Antipov, O. Chmaissem, and M. Marezio, *Nature* 362,226 (1993).
2. A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott, *Nature* 363, 56 (1993).
3. C. W. Chu, L. Gao, F. Chen, Z. J. Huang, R. L. Meng, and Y. Y. Xuen, *Nature* 365, 323 (1993).
4. C. C. Tsuei, A. Gupta, G. Trafas, and D. Mitzi, *Science* 263, 1259 (1994).
5. A. Gupta, J. Z. Sun, and C. C. Tsuei, *Science* 265, 1075 (1994).
6. For recent reviews, see the special issue on high temperature superconductors in *J. Electron Spectrosc. Relat. Phenom.* 66, Nos. 3 & 4 (1994).
7. F. Al Shamma and J. C. Fuggle, *Physics C* 169,325 (1990).
8. R. P. Vasquez, *J. Electron Spectrosc. Relat. Phenom.* 66,209 (1994).
9. P. Almeras, T. Dell'Orto, C. Coluzza, J. Almeida, G. Margaritondo, Y. Y. Xue, R. L. Meng, and C. W. Chu, *J. Appl. Phys.* 76, 1100 (1994).
10. C. S. Gopinath and S. Subramanian, *Physics C* 232,222 (1994).
11. R. P. Vasquez and W. L. Olson, *Physics C* **177**, 223 (1991).
12. D. L. Novikov and A. J. Freeman, *Physics C* **216,273 (1993)**.
13. J. Yu, S. Massidda, and A. J. Freeman, *Physics C* 152,273 (1988).
14. R. P. Vasquez, B. D. Hunt, M. C. Foote, L. J. Bajuk, and W. L. Olson, *Physics C* 190, 249 (1992).
15. J. H. Weaver, H. M. Meyer III, T. J. Wagener, D. M. Hill, Y. Gao, D. Peterson, Z. Fisk, and A. J. Arko, *Phys. Rev. B* 38, 4668 (1988).
16. H. M. Meyer III, D. M. Hill, J. H. Weaver, D. L. Nelson, and C. F. Gallo, *Phys. Rev. B* 38, 7144 (1988).
17. F. Parmigiani, Z. X. Shen, D. B. Mitzi, I. Lindau, W. E. Spicer, and A. Kapitulnick, *Phys. Rev. B* 43, 3085 (1991).

18. R. P. Vasquez, J. Electron Spectrosc. Relat. Phenom. 66,241 (1994).
19. P. Niedermann, A. P. Grande, J. K. Grepstad, J.-M. Triscone, M. G. Karkut, O. Brunner, L. Antognozza, W. Sadowski, H. J. Scheel, and Ø. Fischer, J. Appl. Phys. 68, 1777 (1990).
20. F. Parmigiani and L. Sangaletti, J. Electron Spectrosc. Relat. Phenom. 66,223 (1994).

Figure Captions

1. The O 1s spectra measured from chemically-etched **epitaxial** thin films of (a) **Hg-1212**, and (b) **Tl-2212** (from Ref. 14). The. second derivative of the spectra in (a) and (b) are shown in (c) and (d), respectively.
2. The Hg 4f and **Ba** 4d core level signals measured from **Hg- 1212**.
3. The **Ca** 2p core level signal measured from **Hg- 1212**.
4. The **Cu 2p_{3/2}** core level signal measured from **Hg-12 12**.
5. The valence band and the Hg 5d and Ba 5p shallow core level signals measured from **Hg- 1212**, Below the valence band is the calculated **Cu** 3d partial density of states from Ref. 12. Insets show closeups of the Fermi edges observed after 30s and 60s of etching,
6. Comparison of the valence bands of **Hg-1212** (this work) and **Tl-2212** (from Ref. 11). Below are the calculated apical oxygen partial densities of states of **Hg- 1212** (from Ref. 12) and **TI-2212** (from Ref. 13).











